REPORT DOCUMENTATION PAGE

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
	Technical Paper	

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER 2303
	5e. TASK NUMBER M1A3
	5f. WORK UNIT NUMBER 346127

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048	11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030127 192

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	A		19b. TELEPHONE NUMBER (include area code) (661) 275-5015

2303M1A3

MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)   11 June 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2001-135**
Phillips, Shawn; Haddad, T.S., Blanski, R.L., "Molecularly Reinforced Polymers" (Paper)

2001 International Symposium on Nanocomposites   (Statement A)
(Chicago, IL 25-27 June 2001)(Deadline: 24 June 2001)
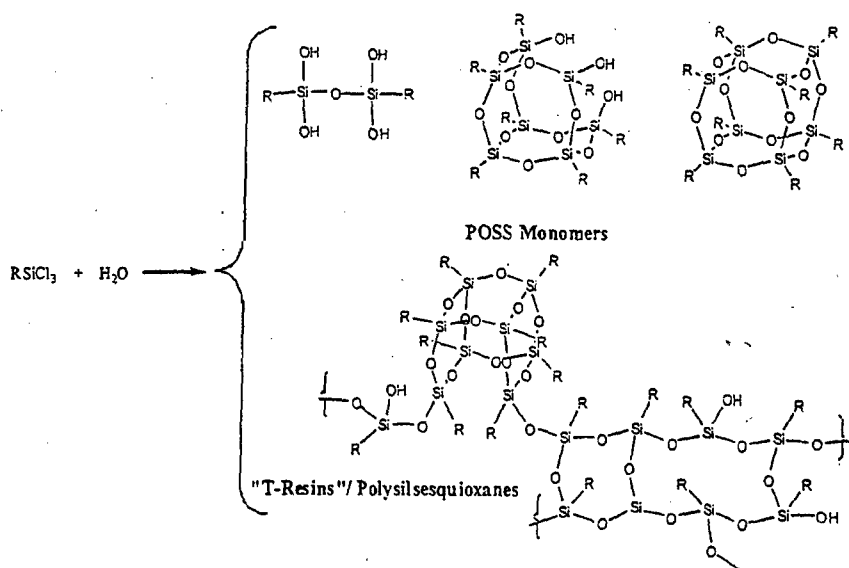
Molecularly Reinforced Polymers

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New nanotechnology initiatives have catapulted nano-materials science to the forefront of research and development in industrial, academic and government labs. While it will be many years before any foreseeable payoffs are realized for new efforts, existing programs have already shown that significant improvements are possible by controlling/understanding the molecular level interactions of polymer systems. For over a decade the Air Force Research Laboratory has invested in both fundamental and applied research of such nanocomposite materials (POSS nanotechnology and clay nanocomposites) and how molecular reinforcement occurs through the addition of inorganic particles, whether blended, grafted, or copolymerized. This talk will broadly cover both nanocomposite materials commercialization efforts, as well as a focused discussion on recent breakthroughs in POSS nanotechnology for controlling polymer property enhancements.

Introduction:

The first report on the self-condensation of alkyltrichlorosilanes ($RSiCl_3$) to yield structurally well-defined silicon oxygen frameworks containing reactive groups has been credited to Brown and Vogt in the mid-sixties while working at GE.[1] Their published results describe the reaction of $CySiCl_3$ with H_2O in acetone to yield a mixture of Polyhedral Oligomeric Silsesquioxanes (POSS) which are continuously isolated over a three-year incubation period (Scheme I). The exact scientific significance of this discovery would not be realized for nearly 15 years.

POSS Monomers

"T-Resins"/ Polysilsesquioxanes
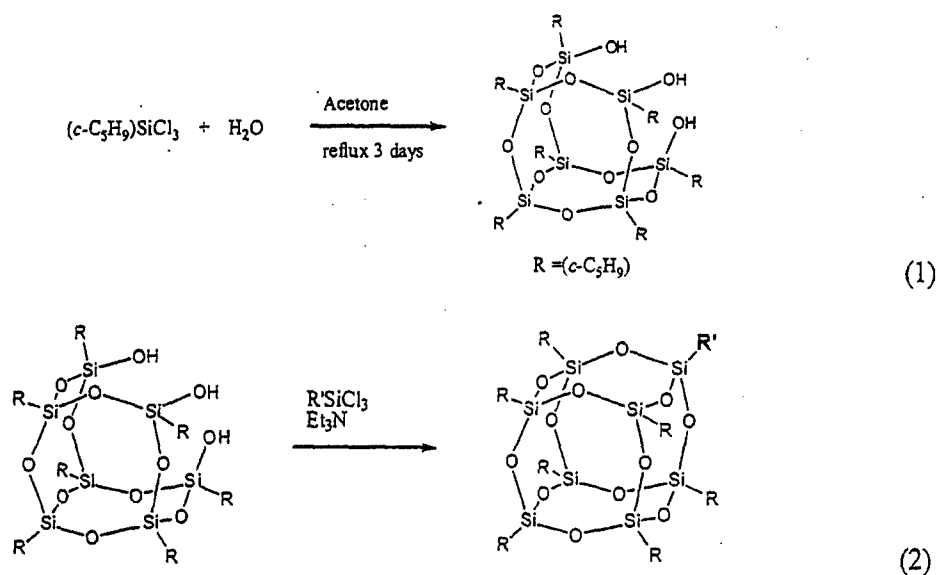
$RSiCl_3 + H_2O \longrightarrow$

Scheme I

In the early eighties POSS-containing materials were gaining popularity, mainly in the Eastern Hemisphere with a 500% increase in yearly silsesquioxane patents and publications from

1980 to 1994 in Japan.[2] The number of known academic researchers were few and included Professor Frank Feher, who wrote a research proposal for using POSS as a model for silaceous surfaces in 1985. His synthesis of a variety of organometallic containing POSS compounds, which repeatedly exhibited high catalytic activity, launched POSS into the forefront of inorganic chemistry (Scheme II).[3] Excellent research by Laine,[4] Roesky,[5] and Hasegawa[6] and the public release of Russian silsesquioxane research helped many professors realize the potential of POSS materials. However, few people outside of academic circles had ever heard of this new nanotechnology. During the early 1990's the research areas for POSS technology had expanded to include the study of POSS incorporation into organic and inorganic polymers by Dr. Joseph Lichtenhan's Polymer Working Group at the Air Force Research Laboratory. The first POSS polymer was a POSS-siloxane bead copolymer, which was tested for space survivability (equation 1).[7] This material exhibited significant atomic oxygen and vacuum ultraviolet radiation resistance with a one-hundred-fold improvement in degradation resistance by forming a passive SiO_2 layer. Early success stories helped create a rapidly expanding niche for new hybrid polymers containing POSS macromolecules.

POSS Monomers:

The limited availability and POSS feedstocks and monomers hampered their progression into Air Force applications. In order to move forward, cheaper and faster routes for POSS synthesis, and the development of new POSS monomers with polymerizable functional groups were required. In 1994 Lichtenhan and coworkers developed a quicker, more efficient synthesis of an incompletely condensed POSS molecule, which reduced the condensation time from 3-36 months to 3 days, and increased the yield from 40 to 65% (equation 1). This was coupled with a patent in 1996 detailing a generic "corner-capping" to yield a variety of polymerizable POSS macromolecules (equation 2).[8]

$$(c\text{-}C_5H_9)SiCl_3 \ + \ H_2O \ \xrightarrow[\text{reflux 3 days}]{\text{Acetone}}$$

R =$(c\text{-}C_5H_9)$

(1)

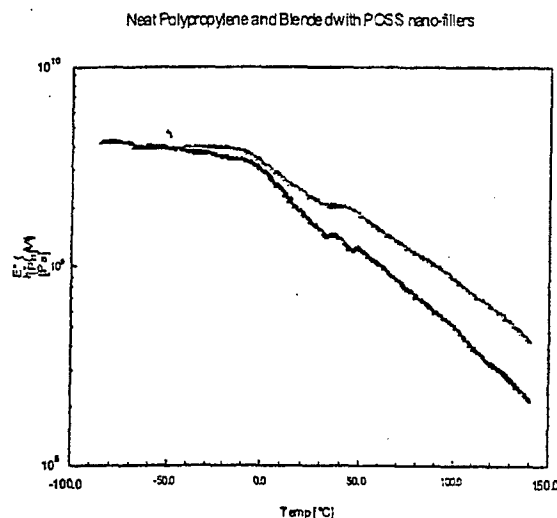$$\xrightarrow{\substack{R'SiCl_3 \\ Et_3N}}$$

(2)

The commercialization of POSS chemical feedstocks began in 1998 with the technology transfer from the Air Force Research Laboratory (AFRL) to Hybrid Plastics and was

strengthened by both a NIST ATP grant and a Cooperative Research and Development Agreement with AFRL. The 2000 Federal Laboratory Consortium Technology Transfer Award was the culmination of the effort that resulted in a significant price reduction and volume increase for POSS feedstocks. Current research efforts are focused on the development of new POSS-polymers and structure/property relationships of existing systems as detailed below.

POSS Molecular Silicas™:

The compatibility of isotactic-polypropylene (iPP) with $(CH_3)_8Si_8O_{12}$ has been well demonstrated by both Lee and Hsiao.[9] Lee's results indicate that iPP with 10 wt% $(CH_3)_8Si_8O_{12}$ showed the most significant improvements in mechanical properties (figure 1); however, loadings of up to 30 wt% were possible without the formation of large POSS aggregates. SWAXS work by Hsiao has shown that only a fraction of the $(CH_3)_8Si_8O_{12}$ is actually molecularly dispersed while the remaining POSS exist as small crystallites. It was further noted that the type of processing equipment used had a dramatic effect on the improvement of storage modulus. High sheer mixers such as twinscrew extruders are preferred over low sheer methods as tested using a brabender.

Neat Polypropylene and Blended with POSS nano-fillers

Figure 1. Nanoreinforced™ polypropylene showing extended heat distortion range of 35 °C.

Additionally, the viscosity of the material with a 10 wt% $(CH_3)_8Si_8O_{12}$ during compounding was reduced from that of the non-reinforced polymer and even higher loadings did not significantly increase the load on the machine (Figure 2). The reduction of melt viscosity is presumably due to the compatibility of the Molecular Silica™ into the polymer.
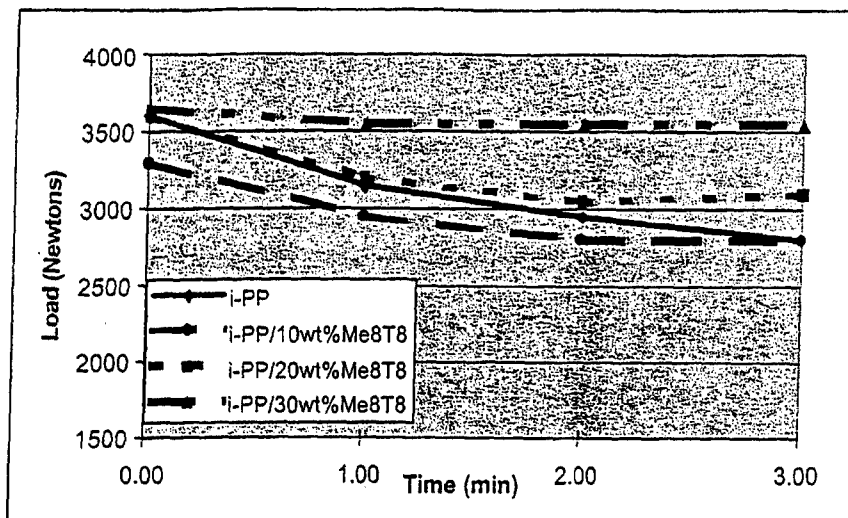
Figure 2. Processing load of nanoreinforced polymer using a DACA™ twinscrew extruder

One of the unique advantages of POSS monomers lies in the ability to functionalize the organic side chains to improve polymer compatibility. The synthetic transformations carried out by Blanski and coworkers indicated that molecular dispersion could be achieved and further resulted in optically transparent materials with loadings as high as 50 wt% of POSS.[10] As can be seen if Figure 3, a solution blending process was employed for the incorporation of $(c\text{-}C_5H_9)Si_8O_{12}$ into 2-million molecular weight polystyrene, resulting in the phase separation of hybrid inorganic/organic material. Full compatibility at 50 wt% POSS loading was observed for $(C_6H_5CH_2CH_2)_8Si_8O_{12}$.
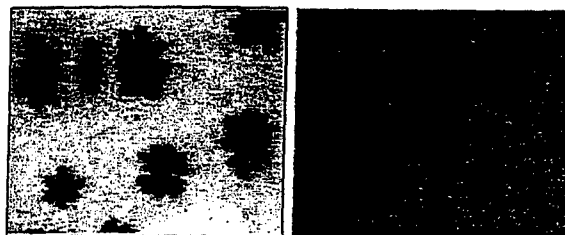

Figure 3. Nanoreinforced™ polystyrene. (a) showing traditional filler heterogeneity Using noncompatible $(c\text{-}C_5H_9)Si_8O_{12}$, (b) optical transparency at 50wt% loading using $(C_6H_5CH_2CH_2)_8Si_8O_{12}$.

POSS™ Copolymers:

While the alloying of POSS Molecular Silicas™ can result in significant improvements in the mechanicals of the polymer system, more dramatic and multi-functional property enhancements have been observed when POSS™ Monomers are copolymerized into polymer systems. The inorganic core of the POSS monomers imparts oxidation and flammability resistance, while the overall size and organic functionalities allow for improved mechanicals due to entrainment with the polymer chains. The variety of POSS monomers that are available allow for significant control of the geometry and solubility in the polymer matrix, while also aiding in the fundamental investigations of structure/property relationships of bead, pendant and cross-linked systems (Figure 4).
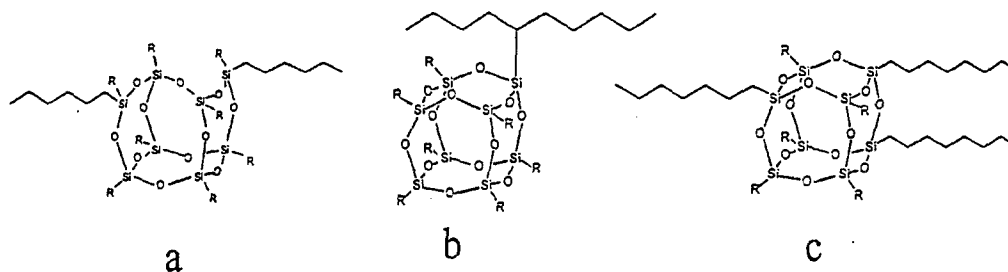
Figure 4. The most common type of POSS-polymers. (a) bead, (b) pendant and (c) cross-linked.

The earliest work on POSS copolymers was reported by Lichtenhan using a difunctional POSS monomer that was co-condensed with short chain polydimethylsiloxane units to form bead-type POSS-PDMS polymers.[11] Changing the wt% POSS incorporation revealed a dramatic linear increase in the glass transition temperature of the polymer system while still retaining the physical properties associated with elastomeric materials (Figure 5). Increasing the siloxane chain length resulted in a significant decrease in the softening temperature, while very short siloxane units displayed a softening temperature around the decomposition temperature. The POSS-PDMS polymers were the first to be studied for oxidation degradation as applied to space-survivable structures in low Earth orbit. Studies in 1996 by Lichtenhan and Gilman and in 2000 by Phillips and coworkers clearly demonstrated the formation of a passivating layer of SiO_2 when exposed to atomic oxygen.[7,12] This layer protected the material from further attack and the homogeneous dispersion of POSS cages throughout the polymer allowed for the healing of cracks and defects.
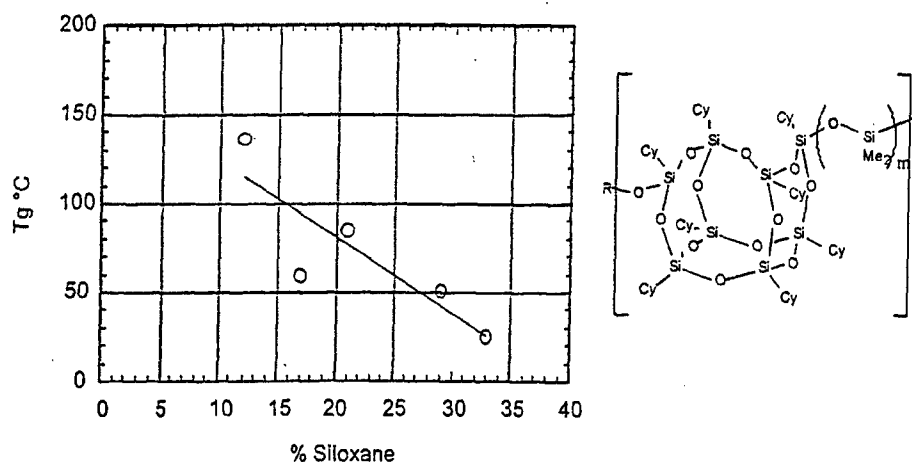

Figure 5. A plot of the wt% siloxane versus T_g, showing that as one decreases the amount of siloxane (or increase the wt% POSS) an increase in T_g is observed.

The most thoroughly studied POSS-polymer system to date for understanding the structure/property relationships of POSS-polymers has been reported by Mather and Haddad.[13] A series of random and block POSS-polynorbornyl polymers with varying wt% of both cyclohexyl and cyclopentyl POSS comonomers were synthesized followed by extensive polymer characterization (equation 3). As expected, the block copolymers exhibited a static T_g for the

non-POSS containing segments and no observable T_g for the POSS blocks. Increases in the T_g and low temperature storage modulus were observed for both types of random copolymers; however, the degree of improvement was more pronounced for the cyclohexyl system (Figure 6).
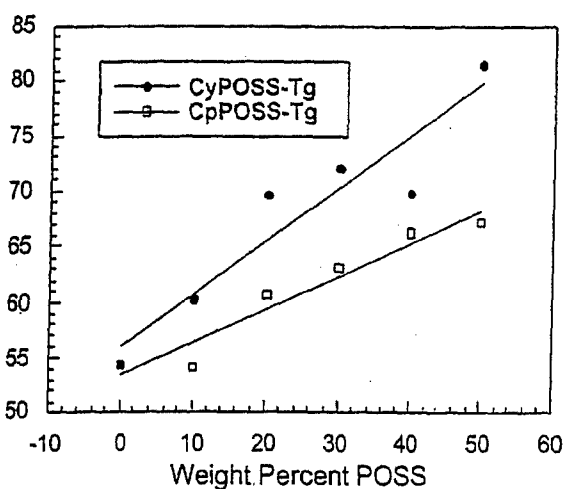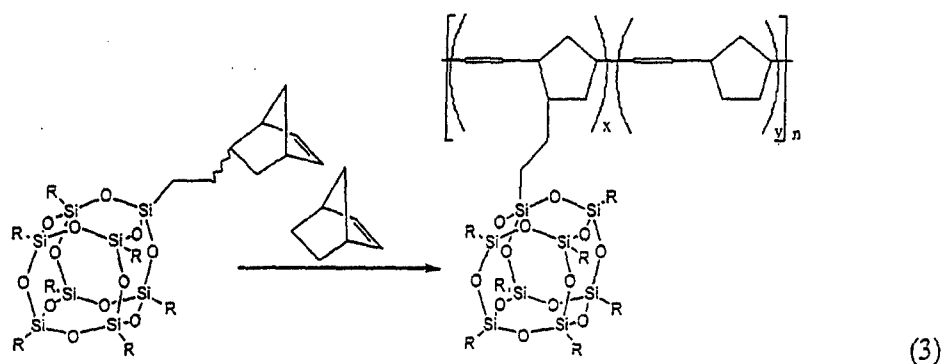

(3)

Figure 6. Plot of wt% POSS versus T_g of copolymer system. The cyclohexyl and cylcopentyl groups are the non-reactive functionalities surrounding the inorganic core.

These differences were attributed to the cyclohexyl groups 'entraining' more of the polymer coils resulting in a stronger interaction with the polymer matrix, while the cyclopentyl groups were less soluble and tended to aggregate into smaller domains (Figure 7). X-ray scattering data of the hybrid polymers also showed a significant ordering of the cyclopentyl derived POSS molecules when compared to the cyclohexyl POSS molecules.
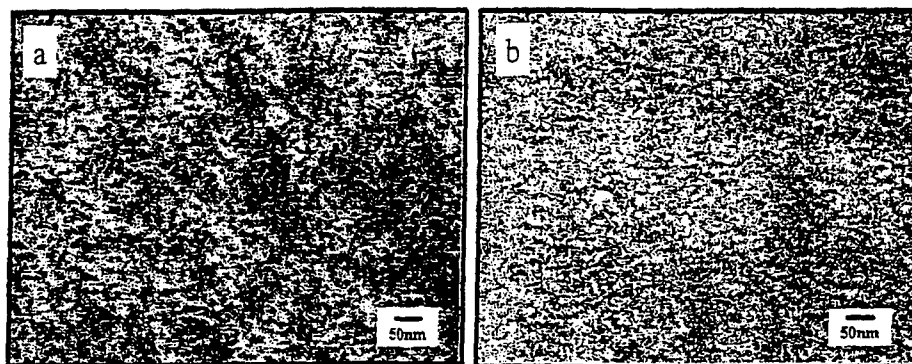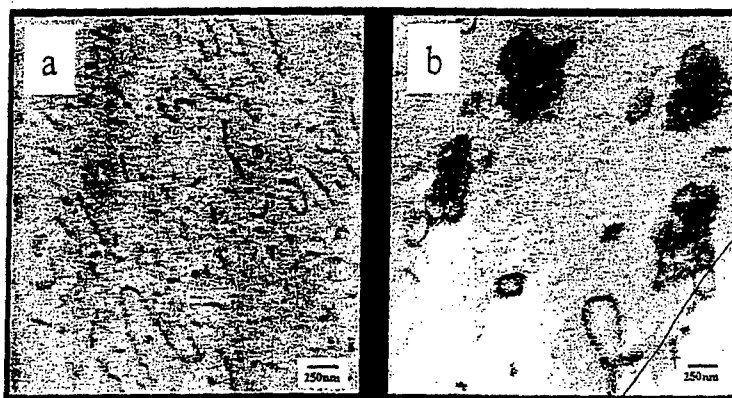
Figure 7. TEM images of random 50 wt% POSS-polynorbornylenes. (a) R = cyclohexyl with 'course' cylinder domains of ~ 12 nm are observed, (b) R = cyclopentyl with 'fine' cylinder domains of 6~nm are observed.

The tendency of the cyclopentyl POSS pendant groups to aggregate is even more pronounced in the TEM images of diblock POSS-polynorbornenes (Figure 8). Farmer's molecular dynamics study on POSS-polynorbornene indicate that aggregation is not required in order for the mechanical improvements to be observed.[14] With Hybrid Plastics recent large-scale production of (i-butyl)$_7$T$_7$(OH)$_3$, a very soluble POSS monomer, it will be interesting to see how complete nanodispersion affects the reinforcing property enhancements of POSS-polynorbornenes.

Figure 8. TEM images of diblock 10 wt% POSS-polynorbornylenes. (a) R = cyclohexyl diblock with POSS in dark regions dispersed throughout the polymer, (b) R = cyclopentyl diblock with significant aggregation of POSS domains.

Linear, segmented polyurethanes are another class of elastomers in which POSS copolymerization has been shown to result in significant property enhancements.[15] Both aliphatic and aromatic POSS diols have been used as chain extenders in a typical approach to polyurethane synthesis (Figure 9). Surprisingly, even with loadings of up to 43 wt% POSS the polyurethane still retained its thermoplastic elastomeric behavior, while also yielding a 200 °C increase in the melt transition temperature and up to a 100 °C increase in the decomposition temperature. *In-situ* SWAXS measurements by Hsiao has shown that the POSS monomer reinforces the hydrogen-bonded hard segments allowing for greater than 400% stretching and a 10x increase in the modulus of the material. Atomic oxygen degradation studies by Phillips and coworkers also showed the formation of a protective SiO$_2$ layer, with the rate of silica formation being directly dependant on the wt% of POSS in the polyurethane.[16]
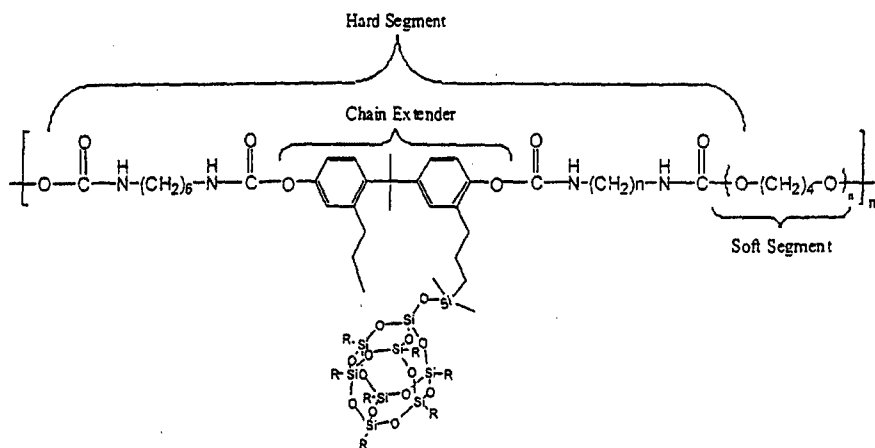
Figure 9

A number of non-elastomeric POSS-polymers have been made, including glassy polystyrenes (PS) and polymethylmethacrylates (PMMA). Aside from the POSS-elastomers, these materials have been studied quite extensively with a clear goal of improving mechanical and physical properties without losing optical clarity. These polymers were made from free radical polymerization of the standard monomer and the functionalized POSS comonomer. Unlike the elastomeric POSS-copolymers, a pronounced increase in T_g is typically not observed. However, dramatic improvements in the use temperature (HDT) are common as tested by both DMTA and TMA (Figure 10).
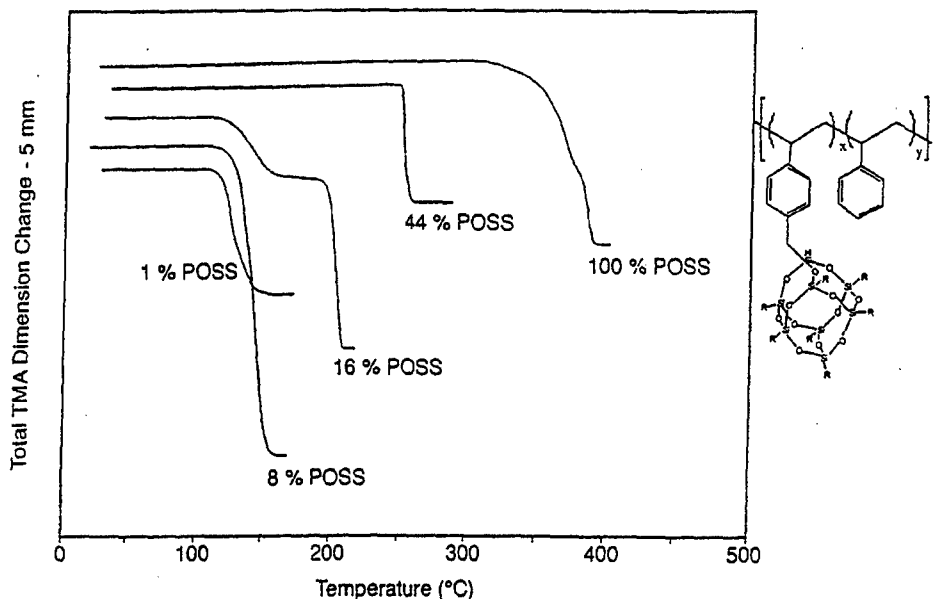

Figure 10. Dimensional changes in the TMA of POSS-polystyrene with increased POSS loadings.

The exact nature of these property enhancements as they relate to the different types of polymer systems is part of an intense tri-collaboration between government, academia and industrial groups leveraging both experimental and computational approaches. The ultimate goal is to be able to predict and control the multiple property enhancements that result from POSS incorporation into a polymer matrix. The first levels of such an understanding have been unraveled, but many more years of basic research will be required in order to reach this goal.

CONCLUSIONS

POSS nanostructured chemicals have been shown to result in dramatic physical and mechanical property enhancements when incorporated into polymers systems. Furthermore, the versatility of the POSS monomers (with over 120 monomers available) allows for an unmatched capability for ensuring compatibility with the chosen polymer matrix. Within the Air Force Research Laboratory a major focus is on developing new POSS-polymers while also investigating the structure/property relationships of existing POSS-polymers with the ultimate goal of controlling/predicting property enhancements. One of the major missions of the Air Force is the transitioning of in-house developed technology. The recent technology transfer to Hybrid Plastics (www.hybridplastics.com) has resulted in significant time and cost reductions along with increases in production resulting in an amplified interest by commercial investors.

ACKNOWLEDGMENTS

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